

Strongly Subspectral Polymeric Series Containing the Cyclobutadiene Moiety

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Summary. Series of strongly subspectral molecular graphs (*i.e.* having a preponderance of common eigenvalues) corresponding to conjugated hydrocarbon polyenes containing cyclobutadiene moieties are presented and their HMO electronic/structural properties are studied. Analytical expressions for these series are derived. The first example of strongly subspectral series containing heteroatoms is presented.

Keywords. Eigenvalues; Heterocyclic; Polycyclobutadienes; Polyenes; Similarity; Subspectral.

Eine stark entartete Reihe aus Cyclobutadieneinheiten aufgebauter polymerer Verbindungen

Zusammenfassung. Eine Reihe stark entarteter (d.h. hauptsächlich gemeinsame Eigenwerte enthaltender) molekularer Graphen von aus Cyclobutadieneinheiten aufgebauten konjugierten Polyenen wird vorgestellt. Ihre elektronischen und strukturellen Eigenschaften (HMO) werden diskutiert, und analytische Ausdrücke für die genannte Reihe werden hergeleitet. Das erste Beispiel einer Heteroatome enthaltenden Reihe von im obigen Sinn entarteten Verbindungen wird präsentiert.

Introduction

The goal of the present investigation is to determine the properties of molecules by identifying elementary substructures (subgraphs) that are carriers of this information in compact form. Examples of elementary substructures are atoms (graph vertices), bonds (graph edges or lines), rings (circuits) [1], excised internal structures (subgraphs spanned by the internal vertices) [2], elementary *aufbau* units (C_4H_2 , C_3H , and C_2) [3], elementary capping units (C_6 , C_5 , C_2 , C , and edge) [4], organic functional groups (subgraphs with a collection of weighted edges and vertices), monomeric units (repeating subgraphs), 1-factor, 2-factor, and *Sachs* subgraphs, *Ulam* subgraphs [1], embedding fragments (*Hall* subgraphs) [5], and right-hand mirror-plane fragments (*McClelland* subgraphs) [6–7]. Excised internal structures and elementary *aufbau* units are important in the enumeration of polycyclic conjugated hydrocarbons, and elementary capping units are important in the generation of fullerene structures. 1-Factor, 2-factor, *Sachs*, *Ulam*, *Hall*, and *McClelland* subgraphs have found application in the determination of eigenvalues (HMO energy levels) and eigenvectors (HMO wave functions) of molecular graphs (vertex-line depictions corresponding to C-C σ -bond skeletons of conjugated

hydrocarbons). Molecular graphs having one or more eigenvalues in common are called subspectral. If they have a preponderance of eigenvalues in common, they are said to be strongly subspectral. An important method for identifying subspectral molecular graphs is the method of *Hall* which he called embedding [5]. Details for the procedure of embedding can be found in several sources [5,7]. For example, if a smaller molecular graph can be embedded in a larger one, then the smaller one is a *Hall* subgraph of the larger one establishing that the latter must have eigenvalues common to the former [5, 7].

Successive attachment of given *aufbau* units under prescribed rules can lead to families (series) of molecular graphs exhibiting characteristic trends. If the smaller members of these families correspond to known molecules, these trends can be used to predict the properties of larger unknown members. Molecules with strongly subspectral molecular graphs are more similar. Beginning with a pair of strongly subspectral molecular graphs, successive attachment of the same *aufbau* unit under certain conditions can lead to a pair of series having a one-to-one correspondence between member molecules of each generation. This approach allows one to systematically study progressive changes in properties among a large number of related molecules that would be difficult to accomplish by other methods.

Results and Discussion

Infinite sets of strongly subspectral series

Figures 1–4 present four sets of series containing molecular graph members that are pairwise strongly subspectral for each successive generation. The eigenvalues listed below each successive pair of molecular graphs are common to both members. Figures 1–4 contain polymers of singly connected monomeric units. Recursion relations for the characteristic polynomials of these series are derived. Similarly, Figs. 5 and 6 presents two sets of triplet series that are strongly

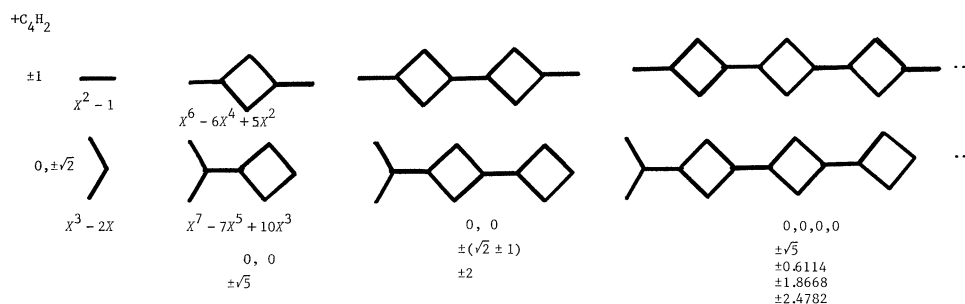


Fig. 1. Two series of molecular graphs that are strongly subspectral; the unmatched eigenvalues are indicated next to the zero generation molecular graphs of ethene and allyl; using the characteristic polynomials listed below the first two molecular graphs of each series, one can determine the characteristic polynomials of the subsequent members by the recursive expression $P_n(X) = (X^4 - 5X^2)P_{n-1}(X) - 4X^2P_{n-2}(X)$

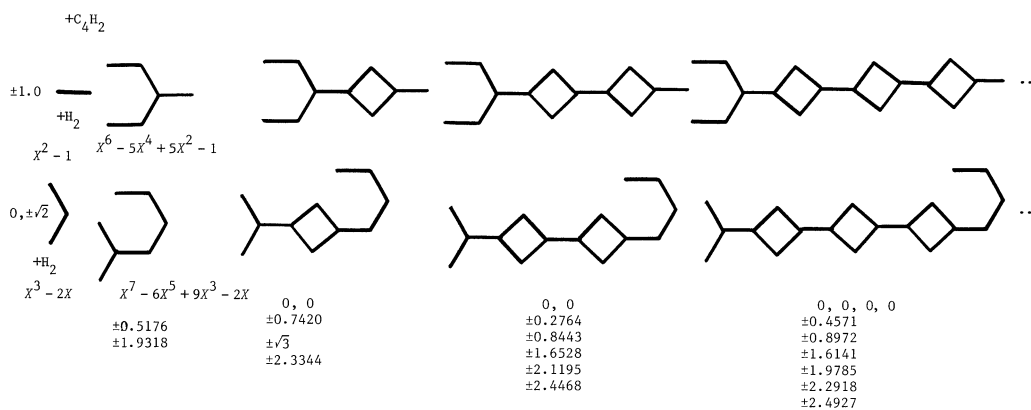


Fig. 2. Two series of strongly subspectral molecular graphs; the unmatched eigenvalues are indicated next to the zero generation members of each series; using the characteristic polynomials listed below the first two molecular graphs of each series, one can determine the characteristics polynomials of the subsequent members by the recursive expression $P_n(X) = (X^4 - 5X^2)P_{n-1}(X) - 4X^2P_{n-2}(X)$

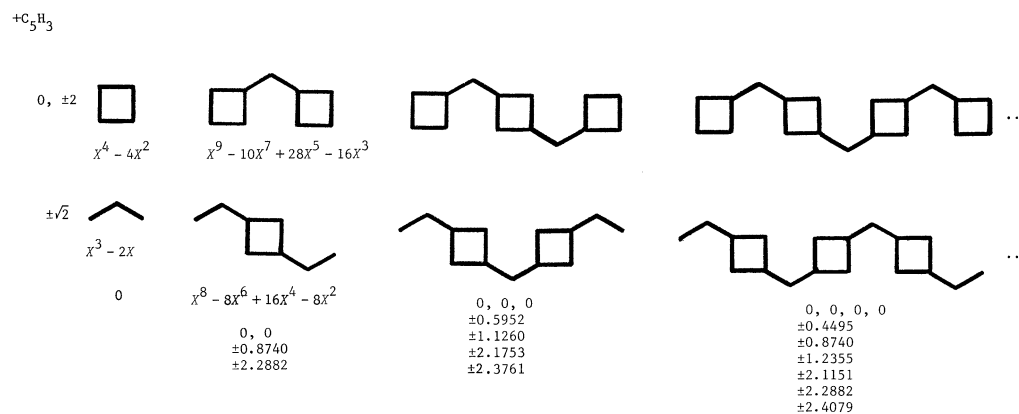


Fig. 3. Two series of molecular graphs that are strongly subspectral; the unmatched eigenvalues are indicated next to the zero generation molecular graphs (cyclobutadiene and allyl); using the characteristic polynomials listed below the first two molecular graphs of each series, one can determine the characteristic polynomials of the subsequent members by the recursive expression $P_n(X) = (X^5 - 6X^3 + 4X)P_{n-1}(X) - 4X^2P_{n-2}(X)$

subspectral. The eigenvalues listed below each successive triplet of molecular graphs are common to all three members. In Fig. 6, the X and Y molecular graph vertices can be CH, CR (R = polyenyl substituent), N, ϕ (the empty set), etc.

The first molecular graphs in the series in Fig 1–4 and 6 are zero generation members, and the eigenvalues affixed next to each are unique to the whole series; the zero generation pair of molecular graphs can be disconnected and need not necessarily be strongly subspectral. The zero generation molecular graphs are frequently *Hall* subgraphs [5–7] for every member of the respective series. The formula of the *aufbau* unit is indicated in the upper left-hand corner of each figure. Although, the smaller corresponding members of a strongly subspectral series can

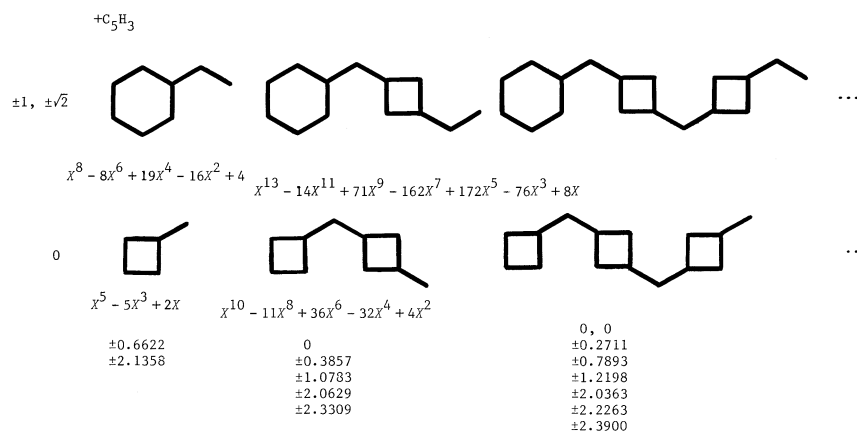


Fig. 4. Two series of molecular graphs that are strongly subspectral; the unmatched eigenvalues are indicated to the left of the first generation member of each series; using the characteristic polynomials listed below the first two molecular graphs of each series, one can determine the characteristic polynomials of the subsequent members by the recursive expression $P_n(X) = (X^5 - 6X^3 + 4X)P_{n-1}(X) - 4X^2P_{n-2}(X)$

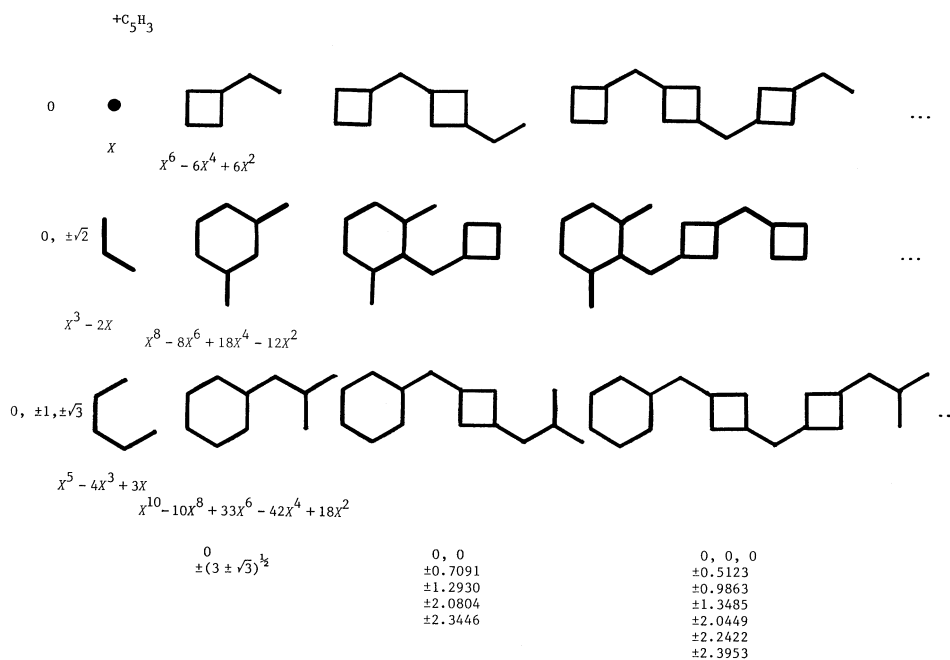


Fig. 5. Three series of molecular graphs that are strongly subspectral; the unmatched eigenvalues are indicated to the left of the first molecular graph (zero generation member) of each series; using the characteristic polynomials listed below the first two molecular graphs of each series, one can determine the characteristic polynomials of the subsequent members by the recursive expression $P_n(X) = (X^5 - 6X^3 + 4X)P_{n-1}(X) - 4X^2P_{n-2}(X)$

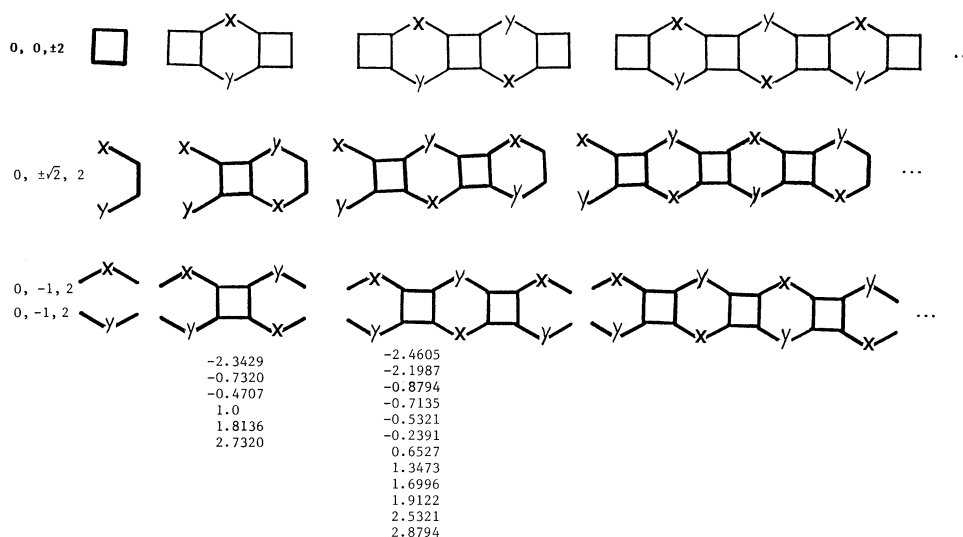


Fig. 6. Three strongly subspectral series of vertex-weighted molecular graphs; the eigenvalues given are for $X = Y$ and $h = k = l$

look quite different, as their size increases they begin to look more similar and in the infinite limit become virtually identical.

The pairs of infinite series tabulated in Figs. 1 and 2 have the same *Hall* subgraphs, ethene and allyl, and all these series devolve to the same infinite limit member. Ethene and 3-methylene-1,4-pentadiene (first generation member in the top series of Fig. 2) are known molecular species, and allyl is a well-known reactive intermediate. 1,3-Dimethylenecyclobutadiene (2nd molecular graph in the upper series of Fig. 1) is a diradical isomer of benzene that has been generated photolytically and studied in a low temperature glassy matrix of 2-methyltetrahydrofuran [8]. Ethene and allyl are zero generation members of the series in Figs. 1 and 2. All remaining molecular graphs in Figs. 1 and 2 correspond to unknown molecules. The characteristic and matching polynomials for the members in the second (lower) series in Fig. 1 have been studied by *Hosoya* [9]. Allyl is also among the zero generation members of the infinite series contained in Figs. 3 and 5. Cyclobutadiene (Figs. 3 and 6) is a transient intermediate [10–11]. The trimethylenemethane, tetramethyleneethane, *m*-xylylene (2nd molecular graph in the middle row of Fig. 5), and cyclobutadiene diradicals and molecules corresponding to the first generation molecular graphs in Fig. 1 have been experimentally and theoretically studied [12–14]. Both 3-methylene-1,4-pentadiene (Fig. 2) and styrene (Fig. 4) are reactive liquids that readily polymerize. Thus, almost all the zero and first generation molecular graphs in Figs. 1–6 correspond to known moderate to very reactive molecules.

The *aufbau* unit for any strongly subspectral pair of series will be either identical but connected differently or strongly subspectral with the same number of vertices. The *aufbau* unit is the same for all four series in Figs. 1 and 2 and may be either cyclobutadiene-1,3-diyl or trimethylenemethanetetrayl; with the former *aufbau* unit, successive generation of the members of these series will involve a

splicing-in operation. 3,4-Dimethylenecyclobutenetetracyl is the *aufbau* unit for the series in Fig. 6 (for $X = Y = \text{CH}$), and methylenecyclobutadienediyl is the *aufbau* unit for the series in Figs. 3–5.

Dimethylenepolycyclobutadiene and related infinite series

The molecular graphs in the upper series of Fig. 1 correspond to the dimethylenepolycyclobutadiene series which has been studied theoretically [13]. Each member of this series is isomeric to a benzenoid acene with the same number of rings. All the molecular graphs in the upper series can be embedded by ethene, and all molecular graphs in the lower series can be embedded by allyl, *i.e.* ethene is a *Hall* subgraph to all members of the upper series, and allyl is a *Hall* subgraph to all members of the lower series. The first generation molecular graph (2^{nd} molecular graph) can be embedded on the third, fifth, seventh, *etc.* generation molecular graphs, the second generation molecular graph can be embedded on the fifth, eighth, *etc.*, and so forth. Everything mentioned for the upper series on embedding applies to the lower series.

The two NBMOs in trimethylenemethane diradical have atoms in common whereas the two NBMOs of the tetramethyleneethane diradical are confined to different sets of atoms. The NBMOs in the former are said to be nondisjoint and in the latter disjoint. Thus, the two NBMOs of trimethylenemethane are degenerate, singly occupied MOs which are orthogonal but coextensive; exchange interaction in coextensive systems favors the high-spin (triplet) state. The first generation member in the upper series of Fig. 1, the 1,3-dimethylenecyclobutadiene diradical, has two nondisjoint NBMOs, and the second generation member, dimethylenedicyclobutadiene, has two disjoint NBMOs. In general, theory predicts that when the number of cyclobutadiene rings in dimethylenepolycyclobutadiene is odd, the corresponding molecule should have a triplet ground state, and when the number of rings is even, a singlet ground state [13]. In the infinite limit, the singlet and triplet states will be degenerate.

The infinite limit members of the pair of strongly subspectral series in Fig. 1 have the same density of states and, as we will see, a zero bandgap. A zero bandgap of an infinite strip is equivalent to a HOMO-LUMO energy difference of zero for a smaller molecule which does not possess a continuum energy levels, and the molecular graphs (except the zero generation members) in Figs. 1–5 have HOMO-LUMO = 0 values of increasing degeneracy as their size increase. The overlapping close proximity of energy levels (continuum) in infinitely large π -electronic networks result in bands bounded by singularities, where the continuum of occupied energy levels is called the valence band, and the continuum of unoccupied energy levels above the valence band is called the conduction band. If there is a zone containing no energy levels between the valence and conduction bands, then this zone is referred to as a bandgap. If this zone contains isolated NBMOs (half-filled zero energy levels), then this polymer network in the bulk phase may possibly form semiconducting, ferromagnetic, or conducting materials depending on the degree of degeneracy which governs the number of charge carriers [9]. This special case has been discussed by *Hosoya* and coworkers [9]. Electrical conductivity in a polymer network is associated with a zero bandgap.

Hosoya and coworkers [15] have shown that the singular points to the density of states of a periodic polymer are given by the eigenvalues of the hypothetical cyclic dimer (sometimes cyclic monomer) having the same recurring *aufbau* unit (unit cell); if this cyclic dimer has NBMOs, then the corresponding periodic polymer has a zero HOMO-LUMO bandgap or isolated NBMOs between the valence and conduction bands [9,15]. To illustrate this, consider the infinite linear polycyclobutadiene strip which is the limit species to the series in both Figs. 1 and 2. The general expression for the infinite polymer ring having the same repetitive (*aufbau*) unit as polycyclobutadiene is $X^4 - 5X^2 - 4X\cos\theta_k = 0$ with $\theta_k = 2k\pi/n$ for $k = 0, 1, 2, \dots, n-1$.

Solution of this equation for the cyclic dimer ($n = 2$) gives eigenvalues $0, 0, \pm 1, \pm 1/2(\sqrt{13} \pm 1)$ which correspond to the singularities for the density of states. Factoring out X from the above equation and setting $X=0$ in the remaining factor gives $\cos\theta_k = 0$. Thus, the infinite polycyclobutadiene polymer has a zero bandgap and is expected to form conductive materials.

Recursion relations for polymers with singly connected monomeric units

All the series in Figs. 1 and 2 devolve to the same infinite limit π -electronic system and have the same following recursion relation

$$P_n(X) = (X^4 - 5X^2)P_{n-1}(X) - 4X^2P_{n-2}(X)$$

where $n=0, 1, 2, 3, \dots$ corresponding to the generation number. Note that $P_0(X) = X^2 - 1$ for the upper series in Figs. 1 and 2 and $P_0(X) = X^3 - 2X$ in the two lower series. $P_1(X)$ differs for all four series in Figs. 1 and 2. The coefficients of $(X^4 - 5X^2)$ and $4X^2$ are determined by the characteristic polynomial of the C_4H_2 *aufbau* unit (cyclobutadienediyl). The characteristic polynomial for the cyclobutadiene monomer is $X^4 - 4X^2$. Since another bond is formed for each attachment of this monomer to the polymer chain and 4 corresponds to the number of edges (bonds) in the C_4 molecular graph, this second coefficient must be incremented by one to give $X^4 - 5X^2$ as the characteristic polynomial for the *aufbau* unit.

The recursion relation for the series in Figs. 3–5 is given by

$$P_n(X) = (X^5 - 6X^3 + 4X)P_{n-1}(X) - 4X^2P_{n-2}(X)$$

where C_5H_3 (methylenecyclobutadienediyl) is the *aufbau* unit. The characteristic polynomial for methylenecyclobutadiene is $X^5 - 5X^3 + 2X$. Since another bond is formed for each attachment of this monomer to the polymer chain and 5 corresponds to the number of edges (bonds) in the corresponding molecular graph, this second coefficient must be incremented by one, and the third coefficient ($a_4 = \frac{1}{2}(q^2 - 9q + 6N_c) - 2r_4 = 4$) [7] must also be amended since it is a function of the number of molecular graph edges (q). Thus, the characteristic polynomial for the methylenecyclobutadienediyl *aufbau* unit is $X^5 - 6X^3 + 4X$.

The $4X^2$ coefficient arises from the way these *aufbau* units are connected which is basically the same for the two different *aufbau* units for the series in Figs. 1–5. An alternative way to acquire these *aufbau* characteristic polynomials is by setting $\cos\theta_k = 0$ in the corresponding prior cyclic dimer expressions. Techniques for finding recursion relations for these type of polymers have been discussed by *Hosoya* [9].

Benzodicyclobutadiene and related infinite series

Three strongly subspectral infinite series are presented in Fig. 6. The first generation member (2nd molecular graph) of the upper series in Fig. 6 is benzodicyclobutadiene if $X=Y=CH$; only one persubstituted derivative of benzodicyclobutadiene has been prepared [16]. In the upper series of Figs. 3 and 6, cyclobutadiene can be embedded on every member of these series, and in the lower series, allyl can be embedded on every other member. In the upper series of Fig. 6 ($X=Y=CH$), benzodicyclobutadiene can be embedded on the third, fifth, seventh, *etc.* generation members, the second generation molecular graph can be embedded on the fifth, eighth, *etc.*, and so forth. This process of progressive embedding of smaller members of an infinite series on larger members can be used to iteratively generate the density of states of the infinite limit member. Also, this iterative process suggests that the eigenvalues of the smaller molecular graphs should have the higher degeneracy in the limit member of a infinite series.

Using *Hosoya's* method [9, 15] the density of states for the infinite limit member to the series in Fig. 6 for $X=Y=CH$ has been determined to be given by the general expression of

$$X^6 - 8X^4 - 4X^3 \cos \theta_k + 12X^2 + 8X \cos \theta_k + 4 \cos^2 \theta_k - 4 = 0$$

which gives eigenvalues of $0, 0, \pm\sqrt{2}, \pm\sqrt{2}, \pm(1 \pm \sqrt{3}), \pm 2$ for the boundaries of the density of states and a zero bandgap. Thus, polybenzocyclobutadiene is expected to be conductive. For the series in Figs. 3–5, the same treatment results in

$$X^5 - 6X^3 + 4X(1 - \cos \theta_k) = 0$$

which gives eigenvalues of $0, 0, 0, 0, \pm\sqrt{2}, \pm 2.0, \pm 2.4495$ for the boundaries of the density of states and a zero bandgap.

The three strongly subspectral series of given in Fig. 6 is perfectly general regardless of the precise identity of X and Y and is the first example of a heterocyclic strongly subspectral series. It should be noted that other triplet-wise matching sets of strongly subspectral series can be generated by simply deleting the X or Y or X and Y vertices in the molecular graphs of Fig. 6.

Design of strongly subspectral series

While the discovery of strongly subspectral series is mainly empirical, some general guiding rules can be summarized. Starting with two empirically found strongly subspectral molecular graphs, search for an *aufbau* unit in which different attachments leads to two successor molecular graphs that are also strongly subspectral. In this search, keep in mind that successive attachments should eventually result in extended systems that begin to look more and more alike, and the retroattachment of this *aufbau* will frequently give zero generation molecular graph members possessing the unique eigenvalues. The zero generation molecular graphs are often embedding fragments for every member of the respective series.

Conclusions

The design of NBMO degenerate systems continues to attract the interest of investigators [17], and the *aufbau* principle in generating strongly subspectral series is

another approach. Subspectrality is one measure of molecular similarity, and the *aufbau* principle can lead to infinite pairs of series whose membership is pairwise strongly subspectral. This provides a strategy for predicting the properties of unknown molecules from known ones if they both have membership to such a pair of series. Furthermore, since the infinite limit members of a strongly subspectral series have virtually the same eigenvalue set, they must have the same density of states.

The results of Figs. 1–6 suggest that end groups have a greater influence on smaller polymer chains than larger ones. The three different infinite polymer strips containing the cyclobutadiene moiety have zero bandgaps and are expected to be conductive.

The first example of a strongly subspectral heterocyclic polymer series is provided by Fig. 6 where X and Y can be any combination of CH, CR (R = polyenyl substituent), N, ϕ (the empty set), *etc.* which complies with good valence.

Coupling *Hosoya's* method of using cyclic boundary conditions in the analysis of infinite linear polymers with our concept of strongly subspectral series allows us to not only determine the precise end points for the density of states but also gives us a another perspective. The simultaneous study of a large group of molecules as performed herein would be prohibitively time consuming using *ab initio* methods, whereas, this approach allows easy discovery of analytical expressions and trends in large groups of related molecules.

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